517g Kinetic Modeling and Parameter Estimation of the Metallocene Catalyzed Slurry Polymerization of Propylene: Effect of Mao/Zr Ratio

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<>Abstract

Homogeneous single site catalysts have dominated the research interest in olefin polymerization over the past 25 years. Sinn and Kaminski [1] started this trend with the discovery that methylaluminoxane (MAO) activates group IV transition metal catalysts. The ability to control regio- and stereochemistries, and comonomer content and distribution are some of the important advantages that metallocene catalysts afford in the polymerization process. A current goal is the reduction of the necessary amount of cocatalyst, typically methylaluminoxane (MAO), since its high cost and the large amounts needed at industrial scale are a barrier to making metallocene systems cost effective with respect to Ziegler-Natta catalysts [2]. In this paper, we study the effect of MAO on reaction rate, molecular weight and polymer microstructure in the slurry polymerization of isotactic polypropylene.

The active catalyst is a cationic species generated in an equilibrium reaction between a zirconocene dichloride catalyst and MAO. Increasing concentrations of MAO shift the equilibrium to the formation of the activated complex. Thus, catalyst activity increases with increasing MAO/Zr ratio [3, 4]. In addition, MAO in solution contains residual trimethylaluminum (TMA) in a typical concentration of 5% wt. It is known that TMA can act as a chain transfer agent leading to the formation of an isobutyl-terminated chain and liberation of the activated complex [5]. In conditions where chain transfer to TMA becomes a competitive process with respect to the other chain transfer reactions, increasing amounts of MAO reduce the molecular weight.

Slurry polymerizations of propylene were carried out using rac-ethylene-bis(1-indenyl)zirconium dichloride/MAO as the catalyst system. Polymerizations were performed at 40ºC in a 500 mL state-of-the-art semi-batch reactor. The effect of MAO/Zr ratio on the rate of reaction, molecular weight and polymer microstructure was explored in order to allow the chain transfer reaction to TMA to be included in our previously developed kinetic model [6]. An exhaustive analysis of end-groups of the polymer chains by ^{1}H and ^{13}C NMR was performed to gain understanding of the chain transfer mechanisms.

Our kinetic model for the homopolymerization of propylene is developed to predict rate of reaction, molecular weight distribution and percentage of unsaturated end-groups of the polymer [6]. It is characterized by: (1) non-instantaneous initiation by insertion of the first monomer molecule; (2) propagation by 2,1 insertion producing a regioerror that lowers the molecular weight through competing chain transfer reactions; (3) chain transfer to TMA; and (4) catalyst deactivation to account for decreasing catalyst activity with time. The estimation of kinetic rate constants was performed using a systematic optimization approach involving on-line measurements of the reaction rate and end-of-batch measurements of molecular weight distribution and polymer end-groups. A least-square objective function was defined to minimize the difference between the experimental measurements and the model predictions. The minimization was performed subject to constraints imposed by the kinetic model equations. These constraints were posed as a set of nonlinear algebraic equations generated by applying temporal discretization techniques to the dynamic model. This presentation will focus on the experimental and modeling results obtained with the rac-ethylene-bis(1-indenyl)zirconium dichloride/MAO catalyst system.

The ultimate goal of this research is to develop a chemically based kinetic model that can be extensible to a number of single-site metallocene catalyst systems. To accomplish this goal, research work with the catalysts *rac*-dimethylsilylbis(2-methyl-4-phenyl-indenyl) $ZrCl_2$ and *rac*-ethylene-bis (4,7-dimethyl-1-indenyl) $ZrCl_2$ is underway. The former species is highly active and stereoselective, while the later species produces isotactic polypropylene with a high frequency of regioirregular 2,1 insertions. Our current work with these catalyst systems will be described in the presentation. <>References 1. Sinn H, W. Kaminsky, H. J. Vollmer, R. Woldt. Living Polymers on Polymerization with Extremely Productive Ziegler Catalysts. Angew. Chem., Int. Ed. Engl. 1980;19(5):390-92.

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